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(54) Title: PROCESS TO PREPARE MEDICINAL AND TECHNICAL WHITE OILS

(57) Abstract: Process for the preparation of medicinal white oil or a technical white oil from a Fischer-Tropsch derived paraffinic distillate bottom product, wherein said bottom product is contacted with a heterogeneous absorbent.



WO 2004/000975 A1

PROCESS TO PREPARE MEDICINAL AND TECHNICAL WHITE OILS

The invention is directed to a process to prepare Fischer-Tropsch derived medicinal and technical white oils. The medicinal white oils preferably have a kinematic viscosity at 100 °C of above 8.5 cSt.

5 Applicants have developed a new process, which is capable of preparing various base oil grades, including high viscosity grades, simultaneously from a relatively heavy Fischer-Tropsch synthesis product. Such a Fischer-Tropsch synthesis product is for example obtainable with the process as described in WO-A-9934917.

10 The new process comprises hydroprocessing of said feed and preferably followed by a pour point reducing step. Such a process is for example described for a different feed in Example 3 of EP-A-776959. The fraction obtained using the more heavier feedstock can in turn be separated by means of distillation, at reduced pressure, into a heavy base oil grade having a kinematic viscosity at 100 °C of at least 8.5 cSt and one or more base oil grades having a kinematic viscosity at 100 °C of between 15 2 and 7 cSt. The heavy base oil grade, which has properties equal or close to those of a technical white oil, will be obtained in a high yield as the bottom product of the distillation.

20 Colour problems are not readily expected when preparing products from a Fischer-Tropsch synthesis product because the Fischer-Tropsch process starts with very pure starting material and because almost no aromatic colour bearing compounds are normally formed. It has been found by applicant that this heavy bottom

distillate fraction, at least in our laboratory set-up, could nevertheless have a slight yellowish colour. Due to this colour the base oil cannot be directly applied as medicinal white oil.

5 Technical and Medicinal white oils are characterized in that they have no colour. Technical white oils have a Saybolt colour (ASTM D-156) of greater than +20. Medicinal white oils have a Saybolt colour of greater than +25, more particularly equal to +30. Other medicinal
10 and technical white oil specifications are a low UV adsorbance at different UV spectral ranges according to for Example FDA 178.3620 (b) and FDA 178.3620 (c) respectively. Medicinal white oils for use in food
15 applications further need to have a kinematic viscosity at 100 °C greater than 8.5 cSt and a 5%w boiling point greater than 391 °C.

 Applicants have now found that by simply contacting a heavy bottom fraction, which does not meet the required specifications for either the technical or medicinal
20 white oil with a heterogeneous adsorbent, a medicinal or technical white oil can be obtained. The invention is therefore directed to the preparation of medicinal white oil or a technical white oil from a Fischer-Tropsch derived paraffinic distillate bottom product, wherein
25 said bottom product is contacted with a heterogeneous adsorbent.

 Examples of suitable heterogeneous adsorbents are active carbon, zeolites, for example natural faujasite, or synthetic materials such as ferrierite, ZSM-5,
30 faujasite, mordenite, metal oxides such as silica powder, silica gel, aluminium oxide and various clays, for example Attapulugus clay (hydrous magnesium-aluminium

silicate), Porocel clay (hydrated aluminium oxide). A preferred adsorbent is activated carbon.

5 In general, activated carbon is a microcrystalline, nongraphitic form of carbon, which has been processed to develop internal porosity due to which it has a large surface area. Activated carbons which have been found particularly suitable, are those having a surface area (N₂, BET method) in the range from 500 to 1500 m²/g, preferably from 900 to 1400 m²/g, and a Hg pore volume in
10 the range from 0.1 to 1.0 ml/g, preferably from 0.2 to 0.8 ml/g. With the expression "Hg pore volume" is meant the pore volume as determined by mercury porosimetry. Very good results have been obtained with activated carbons which additionally have a micropore size
15 distribution of 0.2 to 2 nm with an average of 0.5 to 1 nm, a pore size distribution (Hg porosimetry) in the range from 1 to 10,000 nm, preferably from 1 to 5,000 nm, and a total pore volume as determined by nitrogen porosimetry in the range from 0.4 to 1.5 ml/g, preferably
20 from 0.5 to 1.3 ml/g. Other preferred physical characteristics include an apparent bulk density of from 0.25 to 0.55 g/ml, a particle size of from 0.4 to 3.5 nm, preferably 0.5 to 1.5 nm, and a bulk crushing strength of at least 0.8 MPa, preferably at least 1.0 MPa. Examples
25 of suitable commercially available activated carbons include Chemviron type, Chemviron F-400 (FILTRASORB 400), DARCO GCL 8*30 and DARCO GCL 12*40 (FILTRASORB and DARCO are trade marks).

30 The activated carbon used in the process according to the present invention is preferably dry activated carbon. This means that the water content of the activated carbon should be less than 2% by weight, preferably less than 1% by weight and more preferably less than 0.5% by weight,

based on total weight of activated carbon. This usually means that the activated carbon has to be dried first before application in the process of the present invention. Drying can either be performed ex situ or in
5 situ via conventional drying procedures known in the art. Examples of suitable drying procedures are those wherein activated carbon is dried at a temperature in the range of from 100 to 500 °C for 1 to 48 hours in a nitrogen atmosphere. In case of applying a fixed bed of activated
10 carbon, in situ drying the activated carbon, i.e. drying after the activated carbon has been packed into a bed, is preferred.

 The conditions (temperature, pressure, space velocity) under which the bottom product is contacted
15 with the activated carbon may vary within broad ranges in order to still attain an improved base oil quality. Temperatures in the range of from 20 to 300 °C, preferably 30 to 200 °C, more preferably 40 to 150 °C, have been found to be suitable in this respect. The
20 operating pressure of the process according to the present invention is not particularly critical and may be in the range of from 1 to 200 bar, preferably 1 to 100 bar, most preferably 1 to 20 bar. A suitable weight hourly space velocity has been found to be in the range
25 of from 0.2 to 25 kg/l/hr, preferably from 0.5 to 10 kg/l/hr and more preferably from 1 to 5 kg/l/hr. The process according to the present invention is suitably performed in the absence of added hydrogen.

 High yields of medicinal white oil can be achieved
30 with the following process. Process to prepare a medicinal white oil or technical white oil by:
 (a) hydrocracking/hydroisomerising a Fischer-Tropsch derived feed, wherein weight ratio of compounds having at

least 60 or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch derived feed is at least 0.2 and wherein at least 30 wt% of compounds in the Fischer-Tropsch derived feed have at least

5 30 carbon atoms;

(b) separating the product of step (a) into one or more distillate fraction(s) of lower boiling fractions and a broad range base oil precursor fraction;

(c) performing a pour point reducing step to the broad
10 range base oil precursor fraction obtained in step (b);

(d) isolating a heavy bottom distillate fraction by distilling the product of step (c); and

(e) contacting said bottom distillate fraction with a heterogeneous adsorbent.

15 The relatively heavy Fischer-Tropsch derived feed as used in step (a) has at least 30 wt%, preferably at least 50 wt%, and more preferably at least 55 wt% of compounds having at least 30 carbon atoms. Furthermore the weight ratio of compounds having at least 60 or more carbon
20 atoms and compounds having at least 30 carbon atoms of the Fischer-Tropsch derived feed is at least 0.2, preferably at least 0.4 and more preferably at least 0.55. The Fischer-Tropsch derived feed is preferably derived from a Fischer-Tropsch product which comprises a
25 C₂₀+ fraction having an ASF-alpha value (Anderson-Schulz-Flory chain growth factor) of at least 0.925, preferably at least 0.935, more preferably at least 0.945, even more preferably at least 0.955.

The initial boiling point of the Fischer-Tropsch
30 derived feed may range up to 400 °C, but is preferably below 200 °C. Preferably at least compounds having 4 or less carbon atoms and compounds having a boiling point in that range are separated from a Fischer-Tropsch synthesis

product before the Fischer-Tropsch synthesis product is used as a Fischer-Tropsch derived feed in step (a). The Fischer-Tropsch derived feed as described in detail above will for the greater part comprise of a Fischer-Tropsch synthesis product, which has not been subjected to a hydroconversion step as defined according to the present invention. In addition to this Fischer-Tropsch product also other fractions may be part of the Fischer-Tropsch derived feed. Possible other fractions may suitably be any high boiling fraction obtained in step (b).

Such a Fischer-Tropsch derived feed is suitably obtained by a Fischer-Tropsch process, which yields a relatively heavy Fischer-Tropsch product. Not all Fischer-Tropsch processes yield such a heavy product. An example of a suitable Fischer-Tropsch process is described in WO-A-9934917 and in AU-A-698392. These processes may yield a Fischer-Tropsch product as described above.

The Fischer-Tropsch derived feed and the resulting waxy raffinate product will contain no or very little sulphur and nitrogen containing compounds. This is typical for a product derived from a Fischer-Tropsch reaction, which uses synthesis gas containing almost no impurities. Sulphur and nitrogen levels will generally be below the detection limits, which are currently 5 ppm for sulphur and 1 ppm for nitrogen.

The Fischer-Tropsch product may optionally be subjected to a mild hydrotreatment step in order to remove any oxygenates and saturate any olefinic compounds present in the reaction product of the Fischer-Tropsch reaction. Such a hydrotreatment is described in EP-B-668342. The mildness of the hydrotreating step is preferably expressed in that the degree of conversion in

this step is less than 20 wt% and more preferably less than 10 wt%. The conversion is here defined as the weight percentage of the feed boiling above 370 °C that reacts to a fraction boiling below 370 °C. After such a mild
5 hydrotreatment lower boiling compounds, having three or less carbon atoms and other compounds boiling in that range, will preferably be removed from the effluent before it is used in step (a).

The hydrocracking/hydroisomerisation reaction of
10 step (a) is preferably performed in the presence of hydrogen and a catalyst, which catalyst can be chosen from those known to one skilled in the art as being suitable for this reaction. Catalysts for use in step (a) typically comprise an acidic functionality and a
15 hydrogenation/dehydrogenation functionality. Preferred acidic functionalities are refractory metal oxide carriers. Suitable carrier materials include silica, alumina, silica-alumina, zirconia, titania and mixtures thereof. Preferred carrier materials for inclusion in the
20 catalyst for use in the process of this invention are silica, alumina and silica-alumina. A particularly preferred catalyst comprises platinum supported on a silica-alumina carrier. If desired, the acidity of the catalyst carrier may be enhanced by applying a halogen
25 moiety, in particular fluorine, or a phosphorous moiety to the carrier. Examples of suitable hydrocracking/hydroisomerisation processes and suitable catalysts are described in WO-A-0014179, EP-A-532118 and the earlier referred to EP-A-776959.

30 Preferred hydrogenation/dehydrogenation functionalities are Group VIII metals, such as nickel, cobalt, iron, palladium and platinum. Preferred are the noble metal Group VIII members, palladium and more

preferred platinum. The catalyst may comprise the more preferred noble metal hydrogenation/dehydrogenation active component in an amount of from 0.005 to 5 parts by weight, preferably from 0.02 to 2 parts by weight, per 100 parts by weight of carrier material. A particularly preferred catalyst for use in the hydroconversion stage comprises platinum in an amount in the range of from 0.05 to 2 parts by weight, more preferably from 0.1 to 1 parts by weight, per 100 parts by weight of carrier material. The catalyst may also comprise a binder to enhance the strength of the catalyst. The binder can be non-acidic. Examples are clays and other binders known to one skilled in the art.

In step (a) the feed is contacted with hydrogen in the presence of the catalyst at elevated temperature and pressure. The temperatures typically will be in the range of from 175 to 380 °C, preferably higher than 250 °C and more preferably from 300 to 370 °C. The pressure will typically be in the range of from 10 to 250 bar and preferably between 20 and 80 bar. Hydrogen may be supplied at a gas hourly space velocity of from 100 to 10000 Nl/l/hr, preferably from 500 to 5000 Nl/l/hr. The hydrocarbon feed may be provided at a weight hourly space velocity of from 0.1 to 5 kg/l/hr, preferably higher than 0.5 kg/l/hr and more preferably lower than 2 kg/l/hr. The ratio of hydrogen to hydrocarbon feed may range from 100 to 5000 Nl/kg and is preferably from 250 to 2500 Nl/kg.

The conversion in step (a) as defined as the weight percentage of the feed boiling above 370 °C which reacts per pass to a fraction boiling below 370 °C, is at least 20 wt%, preferably at least 25 wt%, but preferably not more than 80 wt%, more preferably not more than 65 wt%. The feed as used above in the definition is the total

hydrocarbon feed fed to step (a), thus also any optional recycle of the higher boiling fraction as obtained in step (b).

5 In step (b) the product of step (a) is preferably separated into one or more distillate fractions, a base oil precursor fraction having preferably a T10 wt% boiling point of between 300 and 450 °C. A heavy fraction may be separated from the product of step (a) to adjust the resultant viscosity of the medicinal or technical
10 white oil. If no heavy fraction is removed the kinematic viscosity at 100 °C of the white oil may be well above 15 cSt. By adjusting the amount and cut point at which the said heavy fraction is separated from the effluent of step (a) medicinal or technical white oils can be
15 obtained having a kinematic viscosity at 100 °C ranging from 6 cSt cSt to above 25 cSt.

If a heavy fraction is separated then the T90 wt% boiling point of the base oil precursor fraction will preferably be between 350 and 550 °C. The separation is
20 preferably performed by means of a first distillation at about atmospheric conditions, preferably at a pressure of between 1.2-2 bara, wherein the gas oil product and lower boiling fractions, such as naphtha and kerosine fractions, are separated from the higher boiling fraction
25 of the product of step (a). If a high boiling fraction is removed from the product of step (a) as described above, then this higher boiling fraction, of which suitably at least 95 wt% boils above 370 °C, is further separated in a vacuum distillation step wherein a vacuum gas oil
30 fraction, the base oil precursor fraction and the optional higher boiling fraction are obtained. The vacuum distillation is suitably performed at a pressure of between 0.001 and 0.05 bara.

In step (c) the base oil precursor fraction obtained in step (b) is subjected to a pour point reducing treatment. With a pour point reducing treatment is understood every process wherein the pour point of the base oil is reduced by more than 10 °C, preferably more than 20 °C, more preferably more than 25 °C. The pour point reducing treatment is preferably performed by means of a so called catalytic dewaxing process.

The catalytic dewaxing process can be performed by any process wherein in the presence of a catalyst and hydrogen the pour point of the base oil precursor fraction is reduced as specified above. Suitable dewaxing catalysts are heterogeneous catalysts comprising a molecular sieve and optionally in combination with a metal having a hydrogenation function, such as the Group VIII metals. Molecular sieves, and more suitably intermediate pore size zeolites, have shown a good catalytic ability to reduce the pour point of the base oil precursor fraction under catalytic dewaxing conditions. Preferably the intermediate pore size zeolites have a pore diameter of between 0.35 and 0.8 nm. Suitable intermediate pore size zeolites are mordenite, ZSM-5, ZSM-12, ZSM-22, ZSM-23, SSZ-32, ZSM-35 and ZSM-48. Another preferred group of molecular sieves are the silica-aluminophosphate (SAPO) materials of which SAPO-11 is most preferred as for example described in US-A-4859311. ZSM-5 may optionally be used in its HZSM-5 form in the absence of any Group VIII metal. The other molecular sieves are preferably used in combination with an added Group VIII metal. Suitable Group VIII metals are nickel, cobalt, platinum and palladium. Examples of possible combinations are Ni/ZSM-5, Pt/ZSM-23, Pd/ZSM-23, Pt/ZSM-48 and Pt/SAPO-11. Further details and examples of

suitable molecular sieves and dewaxing conditions are for example described in WO-A-9718278, US-A-5053373, US-A-5252527 and US-A-4574043.

5 The dewaxing catalyst suitably also comprises a binder. The binder can be a synthetic or naturally occurring (inorganic) substance, for example clay, silica and/or metal oxides. Natural occurring clays are for example of the montmorillonite and kaolin families. The binder is preferably a porous binder material, for
10 example a refractory oxide of which examples are: alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions for example silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. More preferably a
15 low acidity refractory oxide binder material which is essentially free of alumina is used. Examples of these binder materials are silica, zirconia, titanium dioxide, germanium dioxide, boria and mixtures of two or more of
20 these of which examples are listed above. The most preferred binder is silica.

A preferred class of dewaxing catalysts comprise intermediate zeolite crystallites as described above and a low acidity refractory oxide binder material which is
25 essentially free of alumina as described above, wherein the surface of the aluminosilicate zeolite crystallites has been modified by subjecting the aluminosilicate zeolite crystallites to a surface dealumination treatment. A preferred dealumination treatment is by
30 contacting an extrudate of the binder and the zeolite with an aqueous solution of a fluorosilicate salt as described in for example US-A-5157191 or WO-A-0029511. Examples of suitable dewaxing catalysts as described

above are silica bound and dealuminated Pt/ZSM-5, silica bound and dealuminated Pt/ZSM-23, silica bound and dealuminated Pt/ZSM-12, silica bound and dealuminated Pt/ZSM-22, as for example described in WO-A-0029511 and EP-B-832171.

Catalytic dewaxing conditions are known in the art and typically involve operating temperatures in the range of from 200 to 500 °C, suitably from 250 to 400 °C, hydrogen pressures in the range of from 10 to 200 bar, preferably from 40 to 70 bar, weight hourly space velocities (WHSV) in the range of from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l/hr), suitably from 0.2 to 5 kg/l/hr, more suitably from 0.5 to 3 kg/l/hr and hydrogen to oil ratios in the range of from 100 to 2,000 litres of hydrogen per litre of oil. By varying the temperature between 315 and 375 °C at between 40-70 bars, in the catalytic dewaxing step it is possible to prepare base oils having different pour point specifications varying from suitably -10 to -60 °C.

In step (d) the dewaxed effluent of step (d), optionally after flashing off some low boiling compounds, is separated into one or more low viscosity base oil products and a heavy distillate bottom product. This bottom product is contacted in step (e) with the heterogeneous adsorbent as described above. This bottom distillate fraction may for example meet the specifications of a technical white oil. Thus the present invention is also directed to a method to up-grade a Fischer-Tropsch derived technical white oil to a medicinal white oil by contacting the technical white oil with a heterogeneous adsorbent in the manner described above.

The invention is further also directed to a medicinal white oil having a kinematic viscosity at 100 °C of more than 8.5 cSt, a non-cyclic isoparaffins content of between 80 and 98 wt%, a Saybolt colour of +30, Ultra violet adsorption spectra values as measured by ASTM D 2269 of less than 0.70 in the 280-289 nm spectral band, of less than 0.60 in the 290-299 nm spectral band, of less than 0.40 in the 300-329 nm spectral band and of less than 0.09 in the 330-380 nm spectral band as according to FDA 178.3620 ('c).

The above medicinal white oils may find use as plasticizers or as a mould release process oil. Such mould release agent may find advantageous use in food packaging applications.

The invention will be illustrated by the following non-limiting examples.

Example 1

A bottom distillate fraction having the properties as listed in Table 1 (Feed 1) and as obtained by performing the steps (a)-(d) as described above on a Fischer-Tropsch derived feed was used to prepare a medicinal white oil. The Fischer-Tropsch derived feed used in step (a) was the C₅-C₇₅₀ °C⁺ fraction of the Fischer-Tropsch product, as obtained in Example VII using the catalyst of Example III of WO-A-9934917. The feed contained about 60 wt% C₃₀⁺ product. The ratio C₆₀⁺/C₃₀⁺ was about 0.55.

Table 1

	Feed 1	Feed 2
Kinematic viscosity at 100 °C	7.532	11.11
Density (d20/4)	824.5	831.2
5%w boiling Pt °C	470	479
Pour point °C	-9	-45
Saybolt Colour (ASTM D 156)	-4	
ASTM colour (ASTM D 1500)		L3.0

The bottom distillate fraction was continuously passed over a bed of dry coarse particles of "Chemviron" charcoal type F-400 in upflow mode at 85 °C for about 100 hours, at a rate of 1 g/g.h (about 0.4 l/l.h.).

5 The UV adsorption values and Saybolt colour are listed in Table 2. The results in Table 2 show that a medicinal white oil can be obtained from a Fischer-Tropsch derived bottom distillate fraction. The said
10 distillate bottom product in this Example almost met the technical white oil specifications. The Example thus also shows that a Fischer-Tropsch derived technical white oil can be converted to a medicinal white oil by this simple adsorption process.

Example 2

15 Example 1 was repeated except that Feed 2 was now used. Feed 2 was obtained in a comparable manner as Feed 1. The catalytic dewaxing was performed at a higher temperature such that a lower pour point was obtained for the bottom fraction Feed 2.

Table 2

Property-> fraction:	UV range 280-289 nm	290-299 nm	300-329 nm	330-380 nm	Saybolt colour
Technical white oil specification * (maximum values)	4	3.3	2.3	0.8	> +20
Medicinal white oil specification ** (maximum values)	0.70	0.60	0.40	0.09	+30
Feed 1	1.11	1.65	2.89	0.9	-4
Feed 2	5.0	4.6	5.0	5.4	Too dark to use Saybolt
Oil as obtained in Example 1	0.14	0.10	0.03	0.01	+30
Oil as obtained in Example 2	0.12	0.10	0.06	0.02	+25

* according to FDA 178.3620 (b) as measured by ASTM 2269

** according to FDA 178.3620 ('c) as measured by ASTM 2269

C L A I M S

1. Process for the preparation of medicinal white oil or a technical white oil from a Fischer-Tropsch derived paraffinic distillate bottom product, wherein said bottom product is contacted with a heterogeneous adsorbent.
- 5 2. Process according to claim 1, wherein the adsorbent is active carbon.
3. Fischer-Tropsch derived medicinal white oil having a kinematic viscosity at 100 °C of more than 8.5 cSt.
4. Process according to any one of claims 1-3, wherein
10 said bottom product is obtained by:
 - (a) hydrocracking/hydroisomerising a Fischer-Tropsch derived feed, wherein weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch derived feed
15 is at least 0.2 and wherein at least 30 wt% of compounds in the Fischer-Tropsch derived feed have at least 30 carbon atoms;
 - (b) separating the product of step (a) into one or more distillate fraction(s) of lower boiling fractions and a
20 broad range base oil precursor fraction;
 - (c) performing a pour point reducing step to the broad range base oil precursor fraction obtained in step (b);
 - (d) isolating a heavy bottom distillate fraction by distilling the product of step (c); and
 - 25 (e) contacting said bottom distillate fraction with a heterogeneous adsorbent.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, API Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 179 994 B1 (CLARK JANET R ET AL) 30 January 2001 (2001-01-30) claim 1; figure; examples 1-3; tables 3,5 column 1, line 66 -column 2, line 7 column 9, line 11-60 ---	1-4
X	US 6 332 974 B1 (RYAN DANIEL F ET AL) 25 December 2001 (2001-12-25) claim 1; figure; examples 1-3; tables 1,2 column 1, line 50-65 column 8, line 15-64 ---	1-4
A	GB 815 264 A (FORSCH PATENTVERWERTUNG GES) 24 June 1959 (1959-06-24) claim 1; figure 1 * page 1, lines 28-35 and 74-91 * --- -/--	1-4

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 95 17482 A (MOBIL OIL CORP) 29 June 1995 (1995-06-29) page 2, line 8-23 page 5, line 13-18 page 5, line 34 -page 6, line 8</p>	1-4

INTERNATIONAL SEARCH REPORT

Information on patent family members

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